GOVERNMENT OF INDIA: THE PATENT OFFICE, 214, ACHARYA JAGADISH BOSE ROAD, CALCUTTA-17.

Specification No.112125 Application No. 112125 dated 28th August, 1967. Complete Specification left on 25th June, 1968. Application accepted 25th January, 1969.

INDEX AT ACCEPTANCE—39E[III]

PROVISIONAL SPECIFICATION

SECTION 4

IMPROVEMENTS IN OR RELATING TO CHEMICAL PREPARATION OF SILVER SELENIDE POWDER

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1., INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification describes the nature of this invention:—

This is an invention by CHITTARI VENKATA SURYANARAYANA, Scientist, NARASIMHAN RANGARAJAN, Senior Scientific Assistant KRISHNAMOORTHY NAGARAJA RAO, Senior Scientific Assistant and MARY JULIANA MANGALAM, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens.

This invention relates to chemical preparation of semiconducting silver selenide powder.

In the Schwartz thermopile manufactured by M/s. Hilger & Watts, London, the negative element is made up of 50% silver selenide and 50% silver sulphide. The silver selenide used therein was hitherto prepared only by the method of thermal synthesis taking stoichiometric proportions of silver and selenium in quartz vessel under carefully controlled conditions of vacuum and at a temperature of 1100°C. This is open to the objection that the conditions of synthesis are controlled by several factors mentioned above and costly equipment and careful management. The reproducibility of composition is also rather difficult by the thermal method.

The object of this present invention is to obviate these disadvantages by simplifying the method of preparation by using very in expensive chemical methods at the normal laboratory temperatures and without using any sophisticated techniques.

To these ends, the invention broadly consists in taking a solution of soluble silver salt and adding an aqueous solution of sodium seleno-sulphate. The silver selenide gets precipitated. The precipitate is filtered, washed with very pure distilled water and dried at 110°C. The powder thus prepared has been found to have semiconducting properties exhibiting a reduction in electrical resistance with increase in temperature and has been found to be of n-type. The substance is in soluble in all mineral acids.

The following typical examples are given to illustrate the invention:

Example 1

Sodium-seleno sulphate is prepared by dissolving the required amount of selenium powder in an aqueous solution of sodium sulphite 100 ml of 5% silver nitrate solution was taken to which was added 50 ml of sodium seleno-sulphate prepared by dissolving 2 gms of selenium powder in a solution of sodium sulphite made by dissolving 40 gms in 200 ml water. In cold the silver selenide got precipitated completely and it was filtered, washed with distilled water used earlier and dried at 110°C. The powder exhibited semiconducting properties mentioned earlier.

Example 2

100 ml of 5% silver nitrate solution was taken to which 10 ml of liquor ammonia was added followed by 50 ml of sodium seleno-sulphate solution mentioned earlier. The solution was stirred with a magnetic stirrer until the precipitation was complete in about 20 minutes. It was then filtered, washed and dried at 110°C. The powder thus prepared also showed all the semiconducting properties mentioned earlier though the time for precipitation is slightly longer here. The following are among the main advantages of the invention:

(1) In comparison with thermal method, known hitherto, this method is easy and does not require either costly equipment or attention in controlling factors which are critical in thermal synthesis.

(2) In thermal methods, the concentrations of dopants introduced are subject to various critical factors like the degree of vacuum, the temperature and the vapur pressure characteristics of the constituents etc. Hence a reproducible control of doping concentration is difficult in the thermal method. In this chemical method, the doping concentrations in the bath are easily controlled, and hence its advantage over the thermal method.

Dated this 2nd day of August, 1967.

Dated this 24th day of August, 1967.

Sd./-

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Price : TWO RUPEES

COMPLETE SPECIFICATION

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This is an invention by CHITTARI VENKATA SURYANARAYANA, Scientist, NARASIMHAN RANGARAJAN, Senior Scientific Assistant, KRISHNAMOORTHY NAGARAJA RAO, Senior Scientific Assistant and MARY JULIANA MANGALAM, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian Citizens

This invention relates to chemical preparation of semiconducting silver selenide powder by reactions in aqueous solutions at the laboratory temperature useful in Schwarz thermopiles

Prior knowledge :

In the Schwarz thermopile manufactured by M/s. Hilger & Watts, London, the negative element is made up of 50% silver selenide and 50% silver sulphide The silver selenide used therein was hitherto prepared only by the method of thermal synthesis taking stoichiometric proportions of silver and selenium in a quartz vessel under carefully controlled conditions of vacuum and at a temperature of 1100°C.

Drawbacks connected with hitherto known processes/devices :

The hitherto known method is open to the objection that the conditions of synthesis are controlled by several factors and costly equipment and careful management are needed The reproducibility of composition is also rather difficult by the thermal method

The main object of the invention :

The object of this present invention is to obviate these disadvantages mentioned above by simplifying the method of preparation by using a very inexpensive method namely by bringing about the reactions in aqueous solutions at the laboratory temperature not requiring any sophisticated techniques

The main finding (the new principle) underlying the invention :

The main finding underlying the invention particularly consists in taking an aqueous solution of soluble silver salt and adding an aqueous solution of sodium-seleno sulphate The silver selenid gets precipitated The precipitate is filtered, washed with very pure distilled water and dried at 110°C

The new result flowing from the new finding :

The powder thus prepared has been found to have semiconducting properties exhibiting a reduction in electrical resistance with increase in temperature and has been found to be of n-type The substance is insoluble in cold mineral acids.

A statement (definition) of invention :

The present invention consists of a process for preparation of silver selenide powder, which comprises of silver and selenium elements which consists in reacting in aqueous solution, sodium-seleno-sulphate and a soluble silver salt like silver nitrate, the required silver selenide gets precipitated at the temperature of 30-35°C which when filtered and dried exhibits semiconducting properties

Detailed description .

Sodium seleno sulphate solution is prepared by dissolving metal selenium in aqueous solution of sodium sulphite An aqueous solution of soluble salt of silver, for example, silver nitrate, is made To this, solution of silver nitrate, seleno-sulphate solution is added with continuous stirring as precipitation goes on occurring After sometime the contents are filtered, washed with very pure distilled water and dried at 110°C. The powder thus prepared was found to have semiconducting properties exhibiting a reduction in electrical resistance with increase in temperature and also it was found to be of n-type The substance was insoluble in cold mineral acids.

A few typical examples :

Example 1 :

Sodium-seleno sulphate is prepared by dissolving the required amount of selenium powder in an aqueous solution of sodium sulphite 100 ml of 5% silver nitrate solution was taken to which was added 50 ml of sodium seleno-sulphate prepared by dissolving 2 gms of selenium powder in a solution of sodium sulphite made by dissolving 40 gms in 200 ml water In cold the silver selenide got precipitated completely and it was filtered, washed with distilled water and dried at 110°C The powder exhibited semiconducting properties mentioned earlier. The yield is almost quantitative

Example 2 :

100 ml of 5% silver nitrate solution was taken to which 10 ml of liquor ammonia was added followed by 50 ml of sodium seleno-sulphate solution mentioned earlier The solution was stirred with a magnetic stirrer until the precipitation was complete in about 20 minutes It was then filtered, washed and dried at 110°C. The powder thus prepared also showed all the semi-conducting properties mentioned earlier, though the time for precipitation was slightly longer here Use of ammonia resulted in getting finer particles of the product The yield was almost quantitative

The main advantages of the invention :

The main advantages of the invention consist in its being easier, less costly and requiring less attention which are otherwise not so in the hitherto known thermal method. The thermal method comprises of several critical factors like the degree of vacuum, the temperature of processing, the vapour pressure characteristics of the constituents, etc. which require to be controlled Obviously such critical factors are absent in the present invention

Further, doping, in other words, adding small concentrations of constituents which bring about a remarkable change in the characteristics of silver

selenide will be rather difficult, not easily reproducible and critical to control in the thermal method, which is not at all so in the present method. In that a mere addition of these dopants in the depositing bath will be enough to bring about the same reproducibly.

Summary (Critical discussion):

Silver selenide finds an important use in the Schwarz thermopile manufactured by M/s. Hilger & Watts, London, in which the negative element is made up of 50% silver selenide and 50% silver sulphide. So far the silver selenide used therein used to be synthesied thermally by taking stoichiometric proportions of silver and selenium in a quartz vessel and bringing about the solid state reaction under carefully controlled conditions of vacuum around a temperature of 1100°C. For suitable performance therein silver selenide requires to be doped sometimes with trace elements, which have great effect on the electrical characteristics of the material.

The method of preparation has been highly simplified by the present invention. An aqueous solution of sodium selenosulphate which is easily prepared by dissolving selenium in aqueous sodium sulphite solution and adding the same to an aqueous solution of silver salt results in the precipitation of the required silver selenide. The precipitate only requires to be filtered, washed and dried for further use.

WE CLAIM:

1. A process for the preparation of silver selenide powder, which comprises of silver and selenium elements, which consists in reacting in aqueous solution, sodium selenosulphate and a soluble silver salt like silver nitrate, the required silver selenide gets precipitated at the temperature of 30-35°C which when filtered and dried exhibits semiconducting properties.

2. A process as claimed in claim 1 which comprises the following steps:—

(i) preparation of sodium seleno sulphate solution by dissolving selenium element in an aqueous solvent of sodium sulphite,

(ii) preparation of soluble silver salt solution;

(iii) carrying out the reactions by mixing these two; and

(iv) filtering, washing and drying the powder at about 110°C.

3. A process for the preparation of silver selenide powder substantially as hereinbefore described.

4. Silver selenide powder whenever prepared according to a process substantially as hereinbefore described.

Dated this 21st day of June, 1968.

Sd./-

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GIPN—S3—7(35) CP&D Cal/73—18-8-75—100